SURFACE FOULING: SHORT- VS. LONG -TERM TESTS

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INTRODUCTION

Problems associated with surface fouling of fuel lines, nozzles, and heat exchangers caused by thermo-oxidative stressing of aviation fuel have been documented.[1] With enhanced aircraft performance, heat loads from both the airframe and the engine that must be dissipated via the fuel become greater. The resultant additional fuel degradation exacerbates aircraft system failures. Since the extent of surface fouling depends strongly upon the particular aviation fuel, it is important to be able to assess each fuel in a simple accelerated laboratory test for simulating the thermo-oxidative stress experienced in aircraft fuel lines.

In the present study a simple dynamic test is employed, whereby the fuel is stressed under well-defined chemical-oxidation conditions that are near-isothermal. Quantification of surface and filtered insolubles provides an objective evaluation of fuel behavior at each temperature. In addition, the dependence of deposition rate upon stress duration provides a temporal profile of the reaction. The general laboratory goal is to evaluate fuel at several temperatures in an attempt to simulate thermo-oxidative stress but not the fluid-dynamic conditions in aircraft. These results can then be used to calibrate Computational-Fluid-Dynamics (CFD) models[2] for calculating fouling under the diverse temperature and fuel-flow conditions that are found within aircraft but are difficult to achieve experimentally with small-scale rigs.

The present investigation has involved fouling of heated stainless-steel surfaces caused by a particular Jet-A aviation fuel designated POSF-2827. Although this is a representative fuel that meets USAF specifications, it has a propensity for fouling heated surfaces at low temperatures, making it an ideal candidate for experimental study.[3] Recent results were reported from this laboratory on surface deposition on stainless-steel surfaces as a function of stress duration for fuel flowing through a heat exchanger at 185°C under near-isothermal conditions.[4,5] These results indicated that deposition arises from a bulk-formed species designated a surface-deposition precursor, P, and that deposition is complete within 10 min of stressing inside 0.125-in-o.d. stainless-steel tubing. Deposition over the temperature range 155-225°C was found to occur during a time interval that correlates with the measured time for oxygen consumption.[6,7] The experimental test time in these prior experiments was set at 6 hr to ensure measurable deposits yet maintain surface fouling predominantly on the steel rather than on previously deposited surfaces.

The goal of the current study was to compare deposition in short-term (6-hr) tests with that in long-term tests where most of the deposition occurs on previously deposited surfaces. Results reported here show that the average surface fouling rates measured during extended test times differ from those measured during a 6-hr test. Since the bulk-fuel/wall temperature is held constant during the course of these experiments as a result of the low flow rate, deposits serve only to change the surface layer without influencing the bulk temperature of the fuel.

As the test time is extended, the deposition-rate-versus-stress-duration profile broadens, the maximum is reduced, and its location shifts to longer stress duration. These observations made at 155 and 185°C are shown to arise from a transition in the rate of oxygen loss as a result of surface fouling and a reduction in adherence to a fouled surface. The implications of these findings with respect to inherent surface fouling within aviation fuel systems are discussed.

EXPERIMENTAL

POSF-2827 fuel has a JFTOT breakpoint of 266°C and a sulfur level of 0.079% (w/w). This fuel falls into a category described by Kendall and Mills[8] where the presence of sulfur compounds tends to inhibit oxidation but at the expense of increased insoluble formation.[3]

Data were collected using the Near-Isothermal Flowing Test Rig (NIFTR) which has been described previously.[4,5] The advantage of the NIFTR experiment is the ability to measure deposition rates and dissolved oxygen as a function of reaction time at a fixed temperature. For each selected fuel-flow rate, the reaction time or stress duration is determined by tube dimensions and location along the tube axis. In the present experiment deposits were collected on 0.125-in.-o.d., 0.085-in.-i.d. commercial stainless-steel (304) tubing. The standard heated section was 32 in.; however, for test times longer than 6 hr, the spatial distribution of the deposition broadened and the complete profile could not be collected on a single pass through the heat exchanger. Three approaches were taken: 1) only the limited profile was collected on a single pass, 2) the fuel was passed back through a second tube within the NIFTR to double the path length, and 3) the fuel-flow rate was reduced to extend the stress duration accordingly within a single pass. It is important to distinguish stress duration from experimental test time in dynamic isothermal experiments. Stress duration is the reaction time at temperature, and the experimental test time (along with the fuel-flow rate) determines the total quantity of fuel passed through the system. The total fuel ranged from 25 to 1035 mL. Dissolved oxygen was measured in separate experiments using the entire tube as a reaction region, with stress time being varied by changing the fuel-flow rate.

Deposition rates at 185 and 155°C are based on the quantity of carbon in the deposits determined from surface-carbon burnoff (LECO RC-412) of 2-in. sections cut from the 32-in. heated tube. Rate is expressed in units of micrograms of carbon per unit volume of tube section per unit test time which is equivalent to micrograms of carbon per unit stress time within a tube section per unit volume of fuel passed through the system.[5] In each case the fuel is saturated with respect to air, with oxygen being measured as 64 ppm (w/w).[9]

RESULTS AND DISCUSSION

Deposition. The measured deposition rate averaged for 6, 24, 30, 32, 48, and 69 hr is shown in Figure 1 as a function of stress duration at 185°C for a fixed fuel-flow rate of 0.25 mL/min. The following observations describe the changes in surface deposition with extension of integration time: 1) the profile broadens with significant tailing; 2) the maximum in the deposition rate is reduced; and 3) the center of the deposition peak shifts to slightly longer stress times. Also, the profiles appear to approach a common shape at the longest experimental times. Extended reaction time in the 30- and 69-hr experiments was afforded by a second pass through the heat exchanger. Results of similar experiments at 155°C are presented in Figure 2. The same trends are observed; however, the reaction time frame is extended to permit completion of the deposition processes at lower temperature.

Note that when comparing rates averaged over different experimental times, the baseline drops as the experimental time is increased. Background carbon which is independent of experimental test time has not been subtracted, and its impact is reduced in the longer-term averages.

The major difference between 6-hr tests and those of much longer duration is the nature of the surface. Initially the deposition occurs on cleaned stainless-steel tube surfaces. As the experimental time is extended, the surface gradually makes a transition to a completely carbonaceous-coated one. Deposition should be constant after complete coverage of the stainless-steel surfaces; for example, after the 48-hr test at 185°C, the surface density at the maximum is 90 $\mu g\ cm^{-2}$. The maximum deposition rate per unit area is 1.1 $\mu g\ cm^{-2}$ per hour of experiment. The observed variation in deposition is related to surface changes, and the major factor will be shown to be the rate of oxygen consumption.

Oxygen Loss. The residual dissolved oxygen for this fuel has been reported as a function of reaction time in stainless-steel tubes.[5] Accelerated oxygen consumption observed at higher conversion was attributed to autocatalysis. Figure 3 shows the oxygen loss at 185°C measured using 1) a 32-in. cleaned stainless-steel tube,[5] 2) a tube that previously had been coated with carbonaceous deposits containing 0.27 mg of carbon, and 3) a tube coated with the same deposits containing 1.5 mg of carbon. The initial rates are similar. Autocatalysis causes the rapid increase in rate at higher conversion in the cleaned tube; however, this appears to be a surface-related phenomenon that is no longer observed when the surface becomes coated with deposits. Rates measured with the coated tubes remain constant, indicating a predominantly zeroth-order or oxygen-non-limited reaction.[4] After 8-9 min all of the oxygen is converted, and the source of the deposits (namely, P) can no longer be maintained. This

time corresponds to the location of the maximum in the shifted deposition profile at 185°C. Similarly, oxygen loss measured at 155°C (Figure 4) shows the same trend.

If the stainless-steel tubing is viewed as the norm, then deposits perturb the oxygen consumption by eliminating autocatalysis. If the coated (passivated) tubing is viewed as the norm--an alternative and preferable view--then the stainless steel perturbs the oxygen consumption by providing active catalytic sites which, at higher conversion, lead to an increased oxygen reaction rate. Deposition in short-term (6-hr) tests over the temperature range 155-225°C correlates with oxygen loss measured in cleaned stainless-steel tubes;[6] similarly, deposition in long-term tests is expected to correlate with oxygen loss measured using tubes that have been passivated by deposits. The higher deposition rate observed in 6-hr experiments results from the oxygen loss that occurs during surface-induced autocatalysis. The reduction in surface deposition rate, the broadening of the deposition profile, and the shift in the maximum in the long-term experiments are manifestations of the slower, constant rate of oxygen loss.

The deposition profiles in long-term tests have tails that extend well beyond the region of 100% oxygen conversion. For example, at 185°C, despite complete oxygen depletion at 9 min, the deposition continues beyond 17 min. This is interpreted as reduced surface adherence of P.

Implications. Autocatalysis has been attributed to thermal dissociation of an oxidation product such as hydroperoxide.[5] The present results indicate that autocatalytic effects in POSF-2827 fuel are caused by a surface-induced reaction of an oxidation product involving active sites on stainless steel. Carbonaceous deposits remove active sites, thereby eliminating autocatalysis.

Carbon-burnoff techniques generally require the use of cleaned surfaces for minimizing background. Based upon the current findings, when surface-induced autocatalysis occurs, the maximum deposition and the oxygen reaction rates will be faster in short-term experiments that are carried to high conversion. Fuel evaluation in this laboratory is predicated on accelerated short-term tests that stress the fuel to complete oxygen conversion. In rating fuels, a deposition-rate criterion has not been applied; instead a total integrated quantity of deposit, i.e. the area under the deposition profile in units of micrograms/milliliter, has been used.

Catalytic effects of metals dissolved in fuels, in particular, copper from copper tubing as in Naval applications, can reduce fuel thermal stability, even at low concentrations.[1] Kendall and Mills[8] observed this effect in flask tests, and Morris and Turner[10] observed it in expanded JFTOT experiments. Conceivably, the role of dissolved copper in catalyzing oxygen loss is analogous to the role of stainless-steel walls in what has been termed surface-induced autocatalysis.

Fuel-evaluation techniques such as the JFTOT and Hot Liquid Process Simulator (HLPS) which make use of clean aluminum and stainless-steel surfaces, respectively, would be expected to be sensitive to the nature of the surface and also the manner in which oxygen is consumed. For example, Clark et al.[11] have reported that a metal deactivator (MDA) functions optimally on clean metal surfaces; however, once a lacquer layer has formed, MDA does not reduce deposition. The vulnerability of JFTOT results in short-term tests has been discussed by Clark and Bishop.[12] The initial surface-passivation effects of MDA may mask problems detectable only during extended time periods. In view of the current results, the short-term benefit of MDA may be surface passivation which prevents autocatalysis. The reduced deposition would then be explained in terms of MDA slowing oxygen consumption rather than hindering adherence to the surface. In recent studies the DuPont fuel additive JFA-5 which contains the MDA, N,N'-disalicylidene-1,2-propanediamine, has been found to eliminate autocatalytic oxygen loss in POSF-2827 fuel.[13]

CONCLUSIONS

The dependence of the surface deposition rate of POSF-2827 fuel on isothermal stress duration at 155 and 185°C has been found to be a function of the experimental test time. In short-term (6-hr) tests, initial deposition is governed by the autocatalytic consumption of oxygen. For long-term (~ 70-hr) tests during which the initial stainless-steel surface becomes covered with deposits, the deposition profile changes to one governed by a slower loss of oxygen.

Oxygen loss in cleaned stainless-steel tubes is enhanced at high conversion as a result of surface-induced autocatalysis. After deposits have completely covered the stainless-steel surfaces, active sites necessary for autocatalysis are removed.

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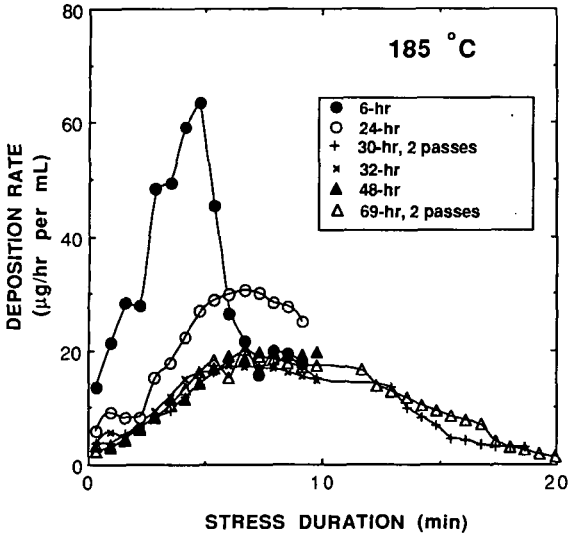

Fig 1. Deposition Rate vs. Stress Duration for POSF-2827 Fuel at 185°C for a Series of Experimental Test Times Measured with a Fuel-Flow Rate of 0.25 mL/min.

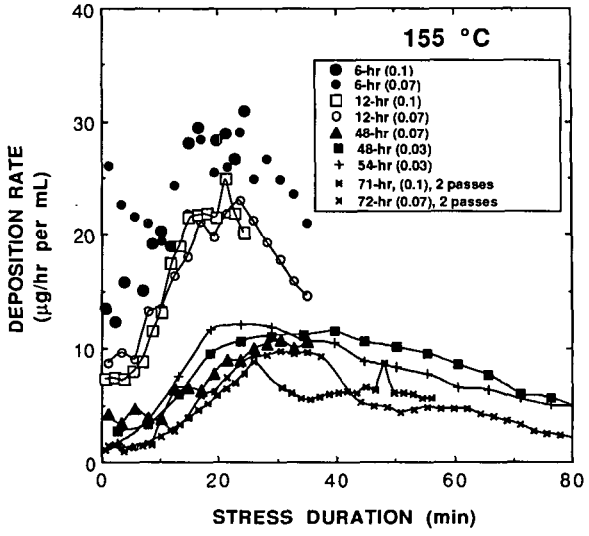

Fig 2. Deposition Rate vs. Stress Duration for POSF-2827 Fuel at 155°C for a Series of Experimental Test Times.

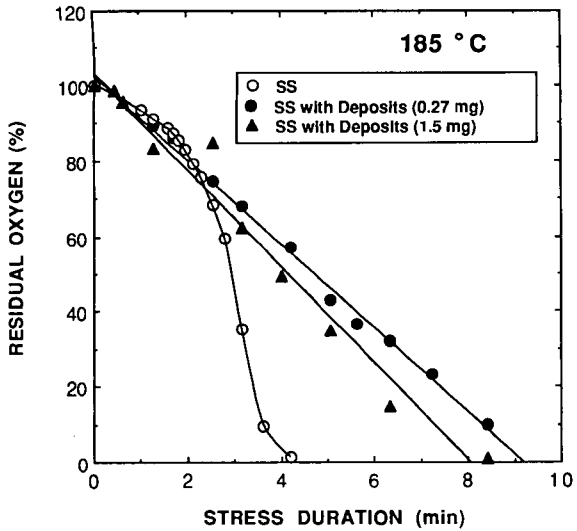

Fig 3. Residual Dissolved Oxygen vs. Stress Duration for POSF-2827 Fuel at 185°C. Measurements Made in 1) Cleaned Stainless-Steel Tubing, 2) Tubing Pre-deposited with 0.27 mg of Insolubles, and 3) Tubing Pre-deposited with 1.5 mg of Insolubles.

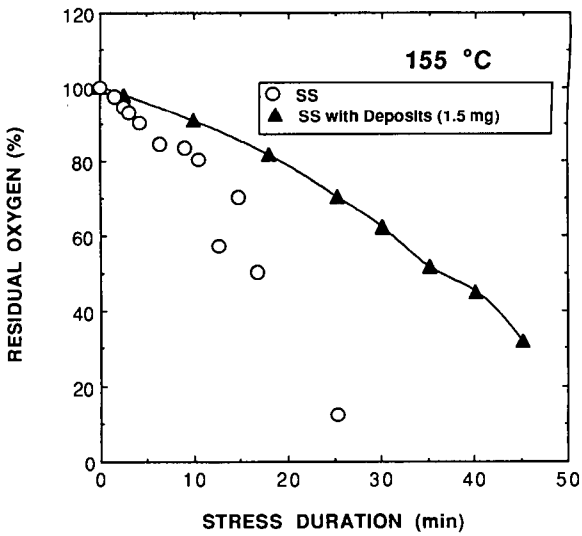

Fig 4. Residual Dissolved Oxygen vs. Stress Duration for POSF-2827 Fuel at 155°C. Measurements Made in 1) Cleaned Stainless-Steel Tubing and 2) Tubing Pre-deposited with 1.5 mg of Insolubles.